Strength and microstructure of colloidal nanosilica enhanced cement pastes.

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Abstract

The macrolevel properties of concrete; strength and durability are dependent on the hydration of cement. The main products of the chemical reactions of cement clinker with water, are calcium silicate hydrates (C-S-H), calcium aluminate hydrates and calcium hydroxide. C-S-H, the major binding and strengthening factor within the hydrating cement paste, is nanosized. Therefore, it is believed that the addition of nanoparticles can modify the characteristics of the C-S-H in nanoenhanced pastes, inducing subsequent alterations at larger scale phenomena. In this research the addition of nanoparticles of silica, referred to as nanosilica (nS) to blended cement formulations was investigated with the aim of enhancing durability and lowering environmental impact. The hydration products, microstructure and compressive strength of the early and later ages (from 1 day until half a year old) hardened cement paste were compared in a series of cement pastes. The reference paste contained Portland limestone cement and additional limestone (summing up to 60% Portland cement and 40% limestone by mass) and the nS enhanced pastes contained nanosilica at 0.1%, 0.5%, 1% and 1.5% by mass of solids. The water to binder ratio was kept constant at 0.3. The size of nanosilica was confirmed by transmission electron microscopy to be in the order of 8 nm to 50 nm, diameter. Performance evaluation of the pastes, indicated that nS exhibits a pozzolanic behaviour consuming calcium hydroxide to form additional C-S-H. Additionally, for pastes with 40% substitution of cement by limestone, low nS content (0.1% to 0.5%) is favouring strength gain even at later ages. Thermogravimetric analyses and scanning electron microscopy provided a further justification of the above hypothesis. The research reported was part of a much broader research project supported by the EU, and involving industrial and academic partners throughout Europe, to investigate nanotechnology enhanced cements.

Introduction

Cement production has raised environmental concerns with regards to the CO_2 emitted during Portland cement clinkering. The total contribution of the cement industry to the global manmade CO_2 emission reaches 8%, not taking into account the energy consumed for the rest of the industrial processes (Meyer, 2009). It has, therefore, become a priority to develop cements in which Portland cement clinker is limited to the maximum, primarily by substituting it with materials, such as fillers, for instance limestone, and/or pozzolanic by-products, for example fly ash or microsilica.

The need for sustainability in construction is calling for more durable and more eco-friendly concretes and consequently cements. Knowing the application for which a concrete is intended (exposure conditions, use, availability of raw materials, and others), the cement paste, which is a highly engineered material, can be designed to meet specific requirements in terms of properties and performance. It can therefore become "greener" not only through the process of replacing Portland cement by supplementary cementitious materials but also by creating a novel blend of constituents that improves the durability and the life span of structures. In this way, cement science can provide the bridge between structural design and protection of natural resources especially taking into consideration the world-wide concern with respect to the deterioration of concrete structures and the need to preserve them for longer periods. This requirement has sparked research towards understanding the internal structure of cement and investigating the modifications applicable in the sub-micron to nanolevel.

Recent researches have demonstrated that using nanoparticles, has a significant effect on the chemical reactions taking place during cement hydration with effects at the macro level; that is to say, mechanical characteristics and durability of the hardened cement paste. The main reason for such modifications in the material behaviour as it decreases to the nanosize is that the specific surface area is multiplied. The nanoparticles are more chemically reactive, since a greater surface area is available for reactions (Oltulu and Sahin, 2011), and they strengthen the nanostructure by minimising the nanosized pores (0.5 to 5 nm wide) within the calcium silicate hydrates.

The addition of nanoparticles in cement mixes opens a new horizon to the research and industry, to the extent that nanotechnology is considered, as the next industrial revolution (Sobolev *et al.*, 2006). This is because the manipulation of matter at the nanolevel has been achieved and observation of the resulting changes at the nanolevel can also be realized. In light of this, nanotechnologically enhanced cement composites can be engineered to exhibit improvements in strength and durability (Raki *et al.*, 2009). Some of the nanoparticles more extensively researched in the cement industry are titanium dioxide (TiO_2), carbon nanotubes (CNT), nanoalumina (Al_2O_3), nanosilica (SiO_2), nanoclays, nanolimestone and others. With the evolution of nanotechnology researchers

have also gained further insight into the parameters affecting the products of cement hydration, the structure of which is nanosized. Therefore, one of the most stimulating questions to be answered, is what effect the addition of nanoparticles has on the hydration of cement? Are some nanoparticles pozzolanic materials in their own right and therefore produce additional calcium silicate hydrate (C-S-H) responsible for the mechanical strength and the durability of the paste or do they primarily act as nucleation centres/ catalysts for cement hydration? This subsequently raises more questions, such as how does the hydration chemistry change, how are the mechanical properties modified and what would, then, be the optimal proportions in such novel blended cement formulations?

Nanosilica (nS) particles were selected in the current research. However, it is still uncertain what is the optimum dosage of nS in cement, with researchers suggesting dosages ranging from 0.5% (Soleymani, 2012), to 1% (Qing Ye *et al.*, 2007; Sobolev *et al.*, 2009) and even as high as 10% by mass of cement (Li *et al.*, 2004). Furthermore, a maximum limit on nS addition in blended cements has not been determined. Adding to this, some researchers are reporting pozzolanic reactivity of the nS particles, whereas others are supporting the seeding effects of nS. Therefore, the way the nS particles affect cement pastes, both at early and later ages is still uncertain. In the present research, different percentages of colloidal nS were added to a blended cement reference combination. This reference combination comprised of a non pozzolanic blended cement paste and was designed to assess the pozzolanic effect of nS addition and to draw the lower and upper limits of nS addition. A suite of compressive strength tests, thermogravimetric and scanning electron microscopy analyses was carried out and the results are presented and discussed.

Experimental procedure

Materials

The materials used were:

- Portland limestone cement CEMII/A-L42.5, with a limestone content of 14%, conforming to EN 197-1
- Limestone (additional), conforming to EN 197-1
- Colloidal amorphous nS in an aqueous suspension containing about 30% by mass of nS particles

The particle size of the nS in the colloidal solution was further investigated by transmission electron microscopy (TEM) as described in Calabria-Holley et al. (2014).

TEM analysis showed that the diameter of the particles ranged from 8 nm to 50 nm and that they were homogenously dispersed.

Mix design

A non-pozzolanic blended cement containing only Portland limestone cement (with 14% limestone content by mass) and additional limestone (LS) was used as the reference to investigate whether the addition of nS has a pozzolanic effect and which are the minimum or maximum proportions to be used in an effort to maximize strength and durability.

In detail, the reference specimen contained 60% Portland cement (PC) and 40% limestone by mass of solids and any nS added was subtracted by this initial limestone content, as shown in Table 1. The amount of water present in the nS aqueous solution was subtracted by the total amount of water that wold be added according to the water to binder ratio of 0.3. Therefore, the general formula of the matrix of the ternary cement paste mixes was:

PC60/LS(40-x)/ nSx,

Where x = % by mass of nS solids at ranges from 0 to 1.5%.

Table 1. Mix Proportions on Ref-60 - percentage by total mass of solids

Sample	PC (%)	LS (%)	nS (%solids)	W/B
Ref-60 (PC60LS40+0% nS)	60	40	0.0	0.3
PC60LS39.9+0.1% nS	60	39.9	0.1	0.3
PC60LS39.5+0.5% nS	60	39.5	0.5	0.3
PC60LS39+1.0% nS	60	39.0	1.0	0.3
PC60LS38.5+1.5% nS	60	38.5	1.5	0.3

The mixing procedure was as follows. Dry constituents were pre-mixed for 60 seconds. Then, the liquid phases, water and nS suspension, were added and mixed with an automatic dual shaft mixer at 1150 rpm for 3 minutes. The fresh paste was cast into cylindrical moulds of 64 mm height and 32 mm diameter. Specimens were vibrated and were air cured in dry sealed conditions at room temperature for the first 24 hours. Consequently, the specimens were demoulded and immersed in water at 20±2ºC, until the selected ages for compressive strength testing (day 1, 7, 28, 56, 90 and 170). Separate samples of the pastes were kept in sealed, airtight bags to avoid contamination for the first 24 hours, then filled up with water at 20±2 ºC and kept for hydration arrest on day 1, 7, 28, 56, 90 and 170 for chemical or microstructural characterisation.

Compressive strength tests were carried out on up to five specimens per mix. All samples were tested at a loading speed of 0.5MPa/s. The value of strength was obtained from the mean of the specimens tested.

Analytical testing

For the paste characterization, arrest of hydration was performed following two different methodologies: solvent exchange and oven drying as described by Calabria-Holley et al. (2014). For SEM images generation and microstructural investigation, solvent exchange was the technique employed for the arrest of hydration. Isopropanol was selected as the most appropriate solvent according to Zhang and Scherer (2011) and Bye (2011). For thermogravimetric analysis (TGA), an oven drying technique was adopted.

Thermogravimetric analysis (TGA)

TGA was carried out using Setaram TGA92. Each powder sample was placed in an aluminium crucible and heated at a rate of 10°C/min from 20°C to 1000°C in nitrogen atmosphere. Argon was used as the carrier gas.

Scanning electron microscope (SEM)

A suite of SEM analyses was carried out for the best performing pastes in terms of compressive strength, that is to say the PC60LS39.5+0.5% nS and a lower one, PC60LS39+1% nS, additionally to the reference specimen, Ref-60, at the ages of 1 and 28 days. A backscattered electron (BSE) detector was used to capture images of the samples. Samples were analysed as received. No coating was required.

Results and Discussion

The hydration in terms of $Ca(OH)_2$ consumption and the cylinder compressive strength of the pastes was determined and compared. It should be noted at this point, that nS was deducted from the limestone content so that the amount of Portlant cement would remain constant for the whole series and therefore, the $Ca(OH)_2$ produced by the reference paste would be direcly comparable with the $Ca(OH)_2$ consumed by nS in the nS enhanced pastes.

Three different areas as distinguished by the themogravimetric (TG) analyses are of particular interest:

The first one is related to the dessociation of water withing the C-S-H and ettringite, between 110^{o}C and 130^{o}C. It can be postulated that the greater the loss the greater the amount of C-S-H and ettringite was produced within the paste (Figure 1and Figure 2).

The second area of interest is associated with the dehydroxylation of $Ca(OH)_2$ between 440^{o}C and 510^{o}C .The amount of $Ca(OH)_2$ present in the paste at different ages can be

computed by the stoichiometric elaboration of the mass loss results within the specific temperature range (Figure 3).

The third area of interest is the decomposition of $CaCO_3$ known as decarboxylation, occurring between 700°C and 810°C. The amount of $CaCO_3$ present in the paste at different ages can be computed by the stoichiometric elaboration of the mass loss results within the specific temperature range (Figure 4).

TGA results presented in Figure 1 and Figure 2, indicate that the amount of C-S-H present in all nS enhanced pastes was greater than that in Ref-60. Hence, it it is clear that nS must react with and consume $Ca(OH)_2$ at early ages, including the first 24 hours (Figure 1), to produce C-S-H in these pastes.

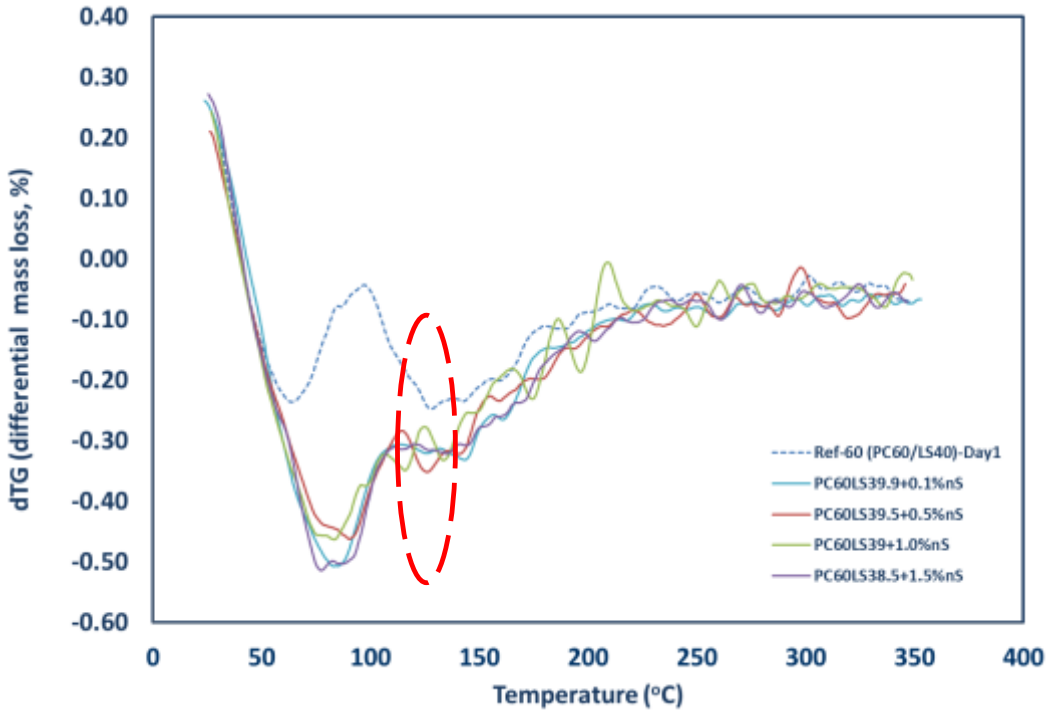

Figure 1. Mass loss related to C-S-H dehydration on day 1, as shown within the dotted area.

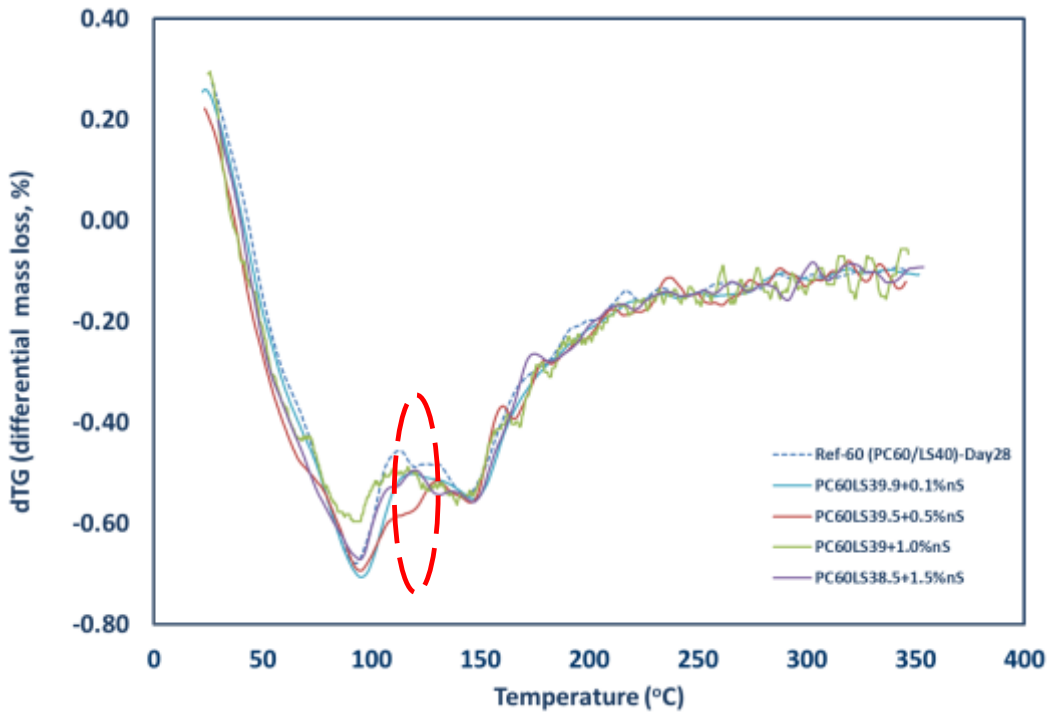

Figure 2. Mass loss related to C-S-H dehydration on day 28, as shown within the dotted area.

With respect to the $Ca(OH)_2$ content, for Ref-60, containing only PC and LS, there was an increase in $Ca(OH)_2$ up to approximately 28 days beyond which it remained constant to day 56, before reducing slightly at day 90 and 170 (Figure 3). Interestingly the $Ca(OH)_2$ at 1 day was equal to 7.9% by mass, and equated to 75% of all $Ca(OH)_2$ produced by the 56 day old paste. Assuming that the curing conditions did not permit carbonation (no significant increase in calcium carbonate content was observed -Figure 4) then it can be argued that for this particular PC, the production of $Ca(OH)_2$ resulting from hydration of alite and belite components of the Portland cement took place rapidly and essentially was completed in the first 28 days, as there was no significant $Ca(OH)_2$ formation after this time. It is worth noting that, $Ca(OH)_2$ consumption amongst the pastes containing over 0.5% nS was practically the same on day 28, providing further evidence that greater than 0.5% nS addition will not be able to react in such pastes. Furthermore, consumption of $Ca(OH)_2$ was practically stabilized by 28 days for the 1% nS addition and by day 56 for the 1.5% nS addition, providing a first indication of a limit reached. On the contrary, both of the lower nS additions, the 0.1% and the 0.5%, exhibited a further 33% consumption of $Ca(OH)_2$ on day 170, relative to day 90. Overall, when nS was present in the paste the amount of $Ca(OH)_2$ at each age was lower than that of the reference mix (Ref-60) and the reduction in the $Ca(OH)_2$ content is prominent up to day 28. Given that in Ref-60 there was no significant $Ca(OH)_2$ formation after 28 days, then it is reasonable to assume that the colloidal nS has been converted to C-S-H

and that there was no further pozzolanic activity after 28 days for the higher nS content pastes. The rapid consumption of small proportions of nS has been observed by a number of authors and is unsurprising given the high $Ca(OH)_2$ to nS ratio and the high surface area of SiO_2 available for reactions.

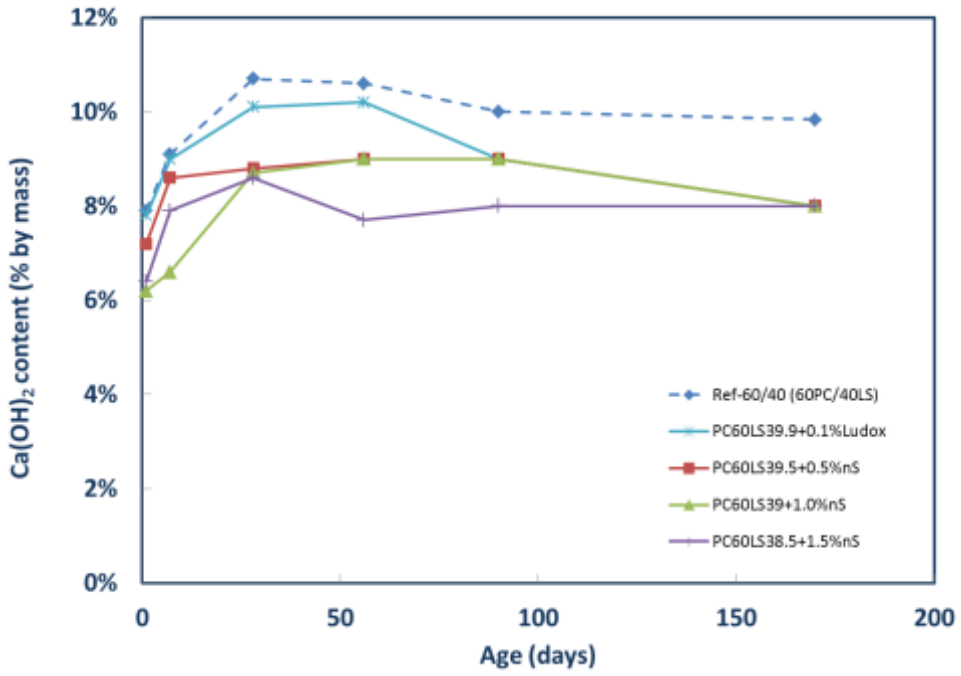

Figure 3. TGA results on Ref-60: of $Ca(OH)_2$ % by mass detected at various ages.

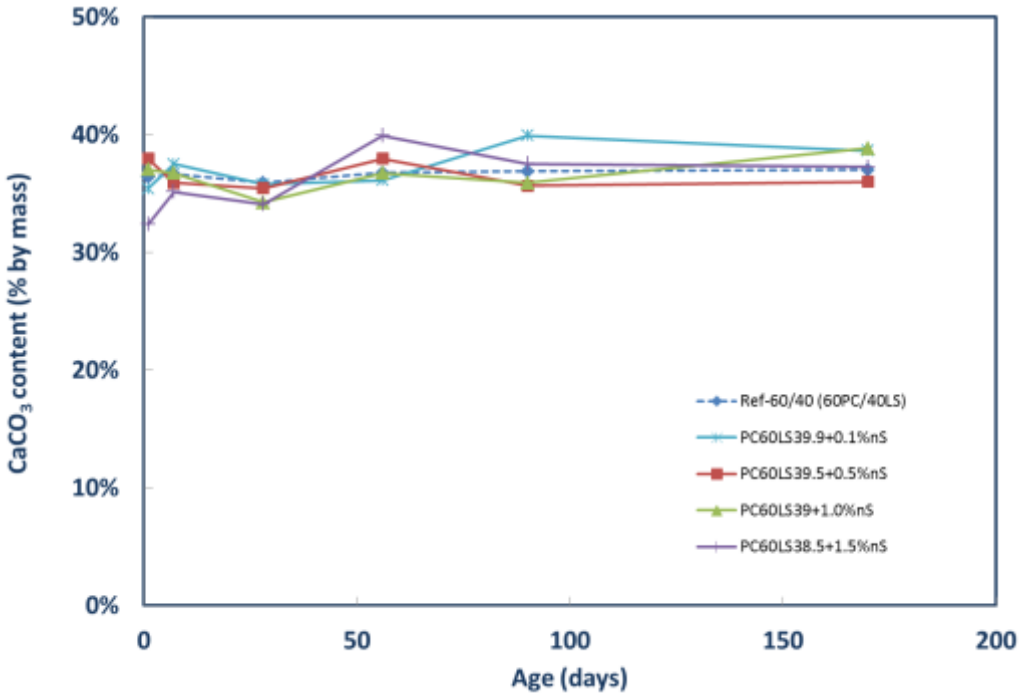

Figure 4. Variation of $CaCO_3$ with time and different nS content.

Figure 5 shows the effect of nS on compressive strength for all pastes as measured between day 1 and day 170. In all cases the nS enhanced pastes showed an improvement in compressive strength when compared to Ref-60. This confirms that nS contributed to the early strength gain, with the higher content (PC60LS38.5+1.5% nS) paste having the highest compressive strength gain at early ages, but the lower strength gain over 56 days of age. The 0.1% and 0.5% nS pastes exhibited the largest overall gain in compressive strength, which could be attributed to a more homogeneous dispersion of the nS particles at lower nS contents – but this requires further investigation.

Based on the results shown in Figure 1, Figure 2 and Figure 5, it appears reasonable to assume that the nS used in this research is a pozzolanic material that consumed $Ca(OH)_2$, and that the additional products resulting from this pozzolanic activity, most probably C-S-H, gave rise to improvements in early age strength and that these strength improvements were maintained at later ages, for the lower (0.1% and 0.5%) nS content pastes. Consequently, nS does not act simply as an accelerator of reactions but plays a role in the development of an enhanced microstructure. There has been much discussion in the literature on the role of nS as providing a nucleation point for C-S-H reactions. Given the research reported in this paper and the significant pozzolanic activity observed, it was not been possible to distinguish between the two mechanisms (nucleation sites and pozzolanic activity) in the early ages. It is very likely that the two mechanisms have taken place at the same time. Further information on the nucleation effects of nS on similar pastes is described in the work by Calabria-Holley *et al.* (2014).

Judging by the TGA and compressive strength results, it can be assumed that a maximum nS content has been achieved, particularly with respect to later age performance. It seems reasonable to suggest that nS additions of less than 0.5% by mass of solids can improve early and late age compressive strength of cement pastes.

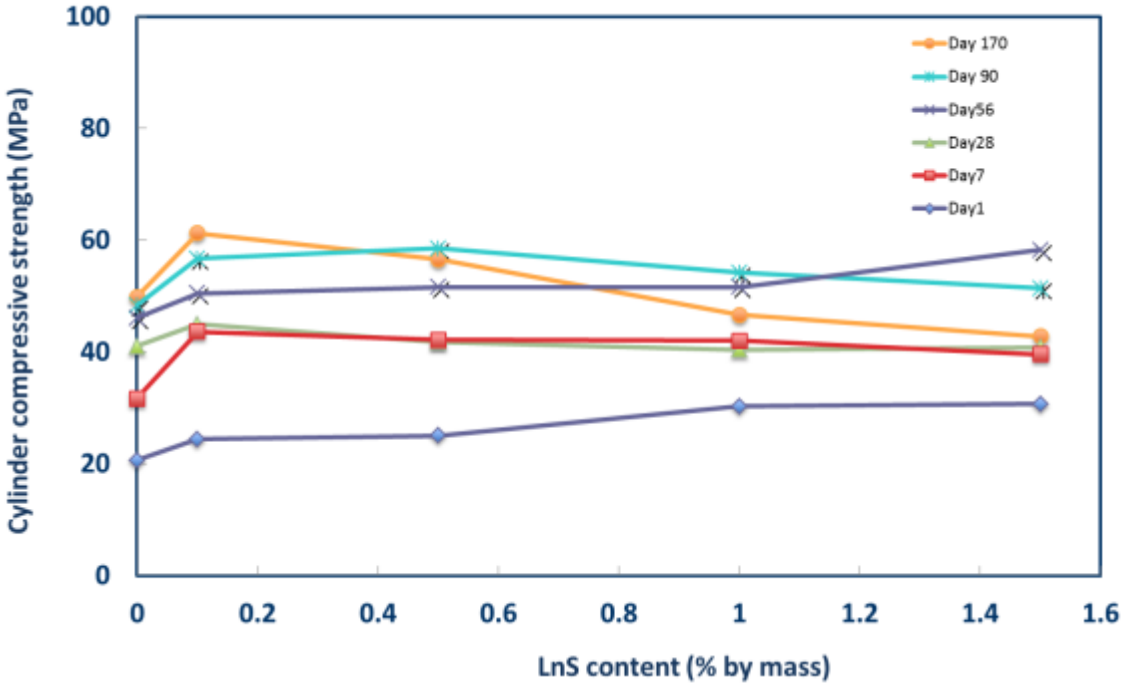

Figure 5. Compressive strength VS nS content PC60%/LS(40-X)%/nS(x%).

Clearly more research is required, but these results potentially provide support to the argument that early-age pozzolanic reactions between nS and $Ca(OH)_2$ may inhibit pozzolanic reactions involving higher amount of nS. The reason for this is that nS reacts instantly with $Ca(OH)_2$ produced by cement hydration, forming dense C-S-H. These dense C-S-H areas are formed around unreacted cement particles and $Ca(OH)_2$ particles, acting as ion penetration barriers, impeding homogeneous hydration of the cement paste and consequently further production of $Ca(OH)_2$ (Figure 7c). As an effect, only a proportion of $Ca(OH)_2$ is available to the pozzolanic reaction, and furthermore the amount of $Ca(OH)_2$ produced could reduce as nS content increases.

The microstucture of Ref-60, PC60LS39.5+0.5%nS and PC60LS39+1.0%nS was investigated after day 1 and 28, which according to the TGA and compressive strength analyses seemed to be the most crititcal, as shown in Figure 6 and Figure 7. All SEM images were back scattered (BS) and were taken at the same magnification (x500). To begin with, on day 1 as depicted in Figure 5, the nS enhanced pastes (Figure 5b and 5c) exhibited patches of what may be considered denser C-S-H areas compared to Ref-60.

These areas are circled in orange. Adding to this, the morphology observed in Ref-60, resembles more PC60LS39.5+0.5%nS than PC60LS39+1.0%nS. In the former, the structure is similar to Ref-60 in terms of visible porosity and amount of $Ca(OH)_2$ crystals, whereas in the later, the paste looks denser with less $Ca(OH)_2$ crystals present, an observation correlating well with the formely presented results.

On day 28, Ref-60 seems more densified, with larger areas of C-S-H present, whereas the morphology between the two nS enhanced pastes exhibits a greater similarity. $Ca(OH)_2$ crystals are more prominant in the higher content nS paste, indicating that nS optimum concentration lays between 0.1% and 0.5%, consuming more $Ca(OH)_2$ to form additional C-S-H, supported by TGA and compressive strength results. Particularly in Figure 6c, it can be noticed that the $Ca(OH)_2$ nest is surrounded by denser C-S-H patches (cirled in orange), possibly rendering its accessibility by nS, difficult. It should be noted that overall, the nS enhanced pastes demonstrated a visibly less porous paste. The observations on the 28 day micrographs, again, correlated well with the previous results, presented.

Conclusions

In this research the performance of nS enhanced, blended cement pastes was investigated with respect to mechanical properties, hydration products formation and consumption and microstructural properties. It was found that 0.5% nS by mass of solids or less may be an optimal dosage for PC/LS pastes that contained no other pozzolanic constituents or superplasticizers. It is possible that because of reactions between the nS and the $Ca(OH)_2$ within the first 24 hours, continuation of the pozzolanic reactions involving the remaining nS particles are less effective at high dosages of nS. It is acknowledged that further work is required. On-going research is investigating the effect that nS has on such pastes when other pozzolanic materials such as microsilica or fly ash are present and the effect on engineering and permeability properties. It would further be of interest to investigate the limits on use of nS in blended binders for concrete rather than pastes, as nS is reported to have beneficial effects in the interface between cement paste and aggregates during early ages (Senff *et al.*, 2010; Ye *et al.*, 2006).

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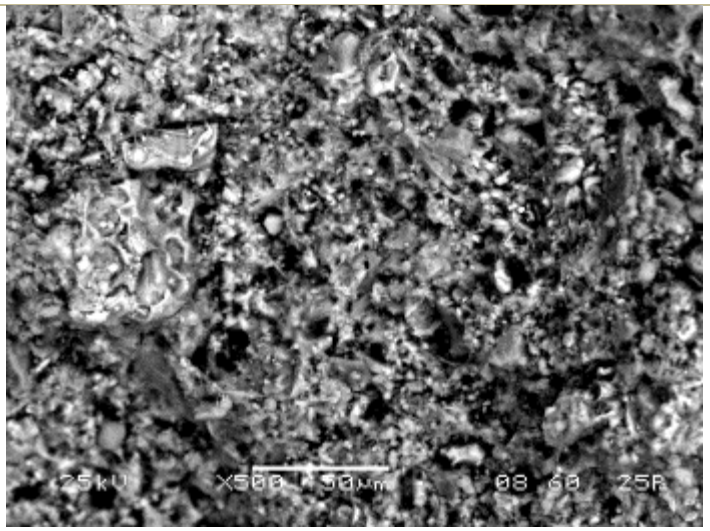
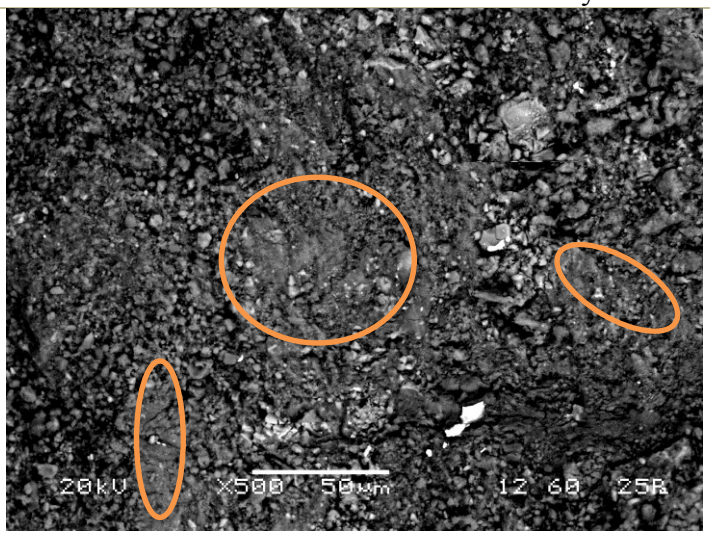


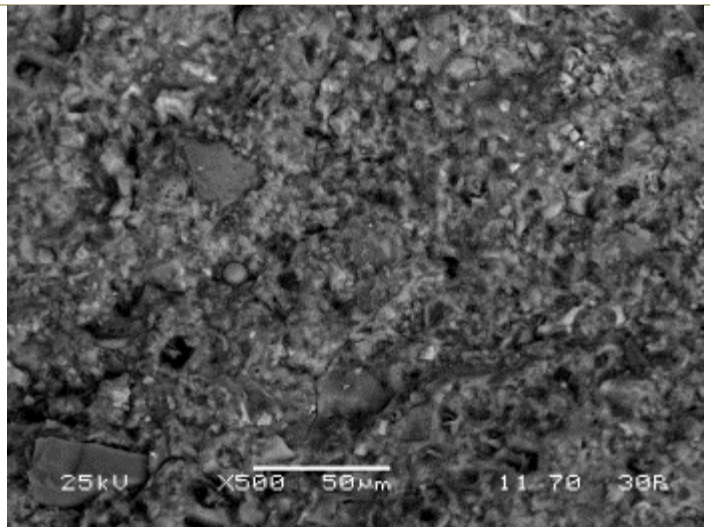
a. Ref-60 (0% nS) -1 Day

b. PC60LS39.5+0.5% nS -1 Day

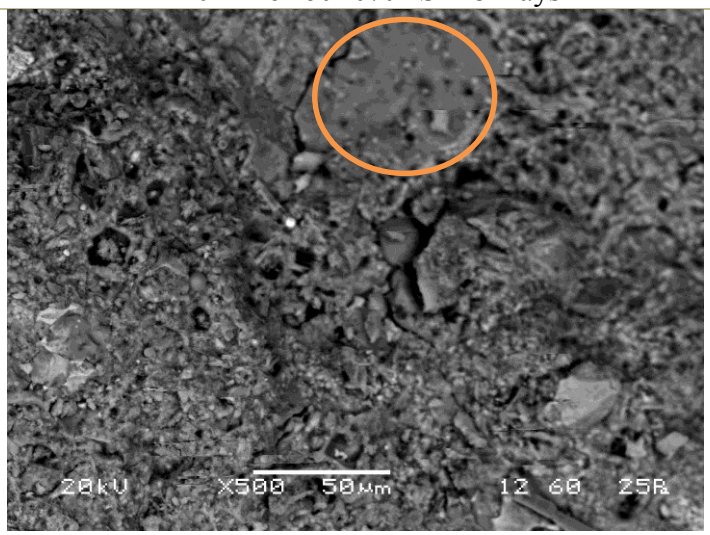


c. PC60LS39 +1.0% nS – 1 Day

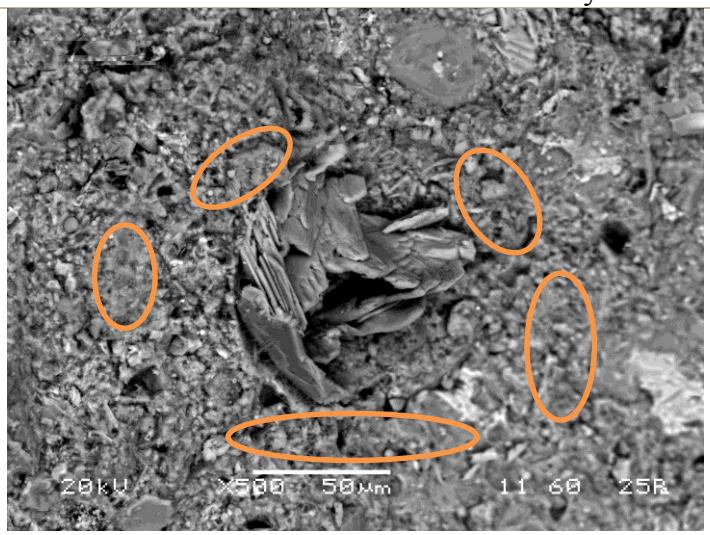
Figure 6. Micrographs of 1 Day old pastes, showing areas of dense C-S-H (in orange circles).



a. Ref-60+0% nS -28 Days



b. PC60LS39.5+0.5% nS -28 Days



c. PC60LS39 +1.0% nS - 28 Days

Figure 7. Micrographs of 28 Day old pastes, showing areas of dense C-S-H (in orange circles).

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